State of New Jersey
Department of Environmental Protection

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DIVISION OF PUBLICLY FUNDED SITE REMEDIATION

STANDARD OPERATING PROCEDURE

TITLE: Standard Operating Procedure (SOP) for Analytical Data Validation of Hexavalent Chromium

REVISION No.:1 _ **ISSUE DATE:** **SOP NO.: 5.A.10**

APPROVED: _____ 10-26-01
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PURPOSE/SCOPE:

This document is the Standard Operating Procedure (SOP) for laboratory data evaluation and validation of Hexavalent Chromium analyzed in accordance with NJDEP Modified USEPA SW-846 Method 3060 and USEPA SW-846 Final Update III (June 1997) Method 7196A.

ORIGINATING ORGANIZATIONAL UNIT (S): **BEMQA**

OTHER ORGANIZATIONAL UNIT (S) AFFECTED: **ALL DPFSR & DRPSR**

Table of Contents

Section **Page No**

I. PURPOSE AND SCOPE: 3

II. AUTHORITY: 3

III. REFERENCE: 3

IV. RESPONSIBILITY: 3

V. POLICY: 3

VI. PROCEDURE: 4

(A) Introduction 4

(B) Data Package Deliverables 5

(C) Preliminary Review 5

(D) Data Validation 5

1. Sample Holding Times 5

2. Instrument Calibration Curve 6

3. Calibration Check Standard (CCS) 8

4. Calibration Blanks (CB) 10

5. Preparation/Reagent Blanks and Field Blanks 10

6. Predigestion Spike Sample Analysis 13

7. Post Verification Spike Sample (PVS) 15

8. Duplicate Sample Analysis 18

9. Laboratory Control Sample Analysis (LCS) 19

10. Sample Result Verification 20

APPENDIX I - GLOSSARY OF TERMS 25

I. PURPOSE AND SCOPE:

This document is the Standard Operating Procedure (SOP) for laboratory data evaluation and validation of Hexavalent Chromium analyzed in accordance with NJDEP modified USEPA SW-846 Methods 3060 and 7196A.

II. AUTHORITY:

This document was prepared and revised under the authority of the Assistant Director of the DPFSR-HSS and the Bureau Chief, BEMQA. This revision, maintenance and use of this document is a work output under the NJDEP Quality Assurance Program Plan. The QA Program Plan was prepared by the NJDEP Office of Quality Assurance and in part by DPFSR-HSS-BEMQA, and was approved by the USEPA Region II.

III. REFERENCE:

This document was prepared based on materials contained in the document entitled: USEPA Office of Solid Waste and Emergency Response Second Edition, and Final Update III (June 1997) - "Test Methods for Evaluating Solid Waste", USEPA SW-846.

IV. RESPONSIBILITY:

The Assistant Director of DPFSR HSS is responsible for the final review and approval of this document. The Chief of BEMQA is responsible for the annual review of this document. The Section Chief of QAS is responsible for the preparation of any revision to this document as well as maintaining QAS staff compliance with this document.

V. POLICY:

The actions contained in this document are the policy of DPFSR-HSS-BEMQA and are derived based on requirements contained in the referenced NJDEP modified USEPA SW-846 Methods 3060 and 7196A.

VI. PROCEDURE:

(A) Introduction

This document is designed to offer guidance in laboratory data evaluation and validation. In some aspects, it is equivalent to a Standard Operating Procedure (SOP); in other more subjective areas, only general guidance is offered due to the complexities and uniqueness of data relative to specific samples.

Those areas where specific SOPs are possible are primarily areas in which definitive performance requirements are established. These requirements are concerned with specifications that are not sample dependent; they specify performance requirements on matters that should be fully under a laboratory's control. These specific areas include laboratory preparation blanks, calibration standards, calibration check standards, and laboratory control standards. Failure to meet these performance requirements warrants that corrective action be taken by the laboratory.

At times, there may be an urgent need to use data that do not meet all QA/QC requirements. Any decision to utilize data for which non-sample specific criteria have not been met is strictly to facilitate the progress of projects requiring the availability of the data and such decisions should be clearly noted in the data validation report. Use of this data does <u>not</u> constitute acceptance of the data in terms of method compliance nor does it release the laboratory from the obligation to perform as per the analytical method. A laboratory submitting data, which are out of specification, may be required to re-run or resubmit data. The only exception to this is in the area of requirements for individual sample analysis; if the nature of the sample itself limits the attainment of specifications, appropriate allowances must be made. An overriding concern of the DPFSR-BEMQA is to prevent non-sample specific data validation requirements from adversely affecting overall data validation activities. There is ultimately no justification for noncompliance on requirements for performance relative to such areas as blanks, calibration and performance verification standards. Ideally, data validation activities should only be concerned with subjects requiring professional judgment on individual sample results.

With these concepts in mind, this document is designed to permit structured data review. To this end, the document is arranged in order, with the most objective, straightforward validation elements given first.

It will be the data reviewer's responsibility to notify the assigned NJDEP Technical Coordinator and Site/Case Manager concerning problems and shortcomings in regards to laboratory data via a Data Validation Report and a Target Analyte Summary List. If mandatory actions are required, they should be specifically noted in a Data Validation Report. This report should also be used to note overall deficiencies requiring attention as well as comments on general laboratory performance and any discernible trends in the quality of data.

(B) <u>Data Package Deliverables</u>

Data generated using NJDEP modified USEPA SW-846, Final Update III Hexavalent Chromium methods must be delivered to NJDEP-DPFSR/DRPSR in the regulatory format as defined in the currently active Professional Laboratory Services Contract and the Technical Requirements for Site Remediation N.J.A.C. 7:26E. Data delivered in the "Reduced Regulatory Format" can only be reviewed against the requirements of this SOP and cannot be validated.

(C) Preliminary Review

In order to use this document effectively, the reviewer should have a general overview of the data deliverable package at hand. The exact number of samples, their assigned laboratory and field identification numbers, their matrix, and concentration level, the identity of any field QC samples (blanks, duplicates, spikes, splits), sampling dates and the name of laboratory involved for the analysis are essential information. Background information on the site is helpful but at times, it is very difficult to locate. The NJDEP Technical Coordinator or the Site/Case Manager is the best sources for answers or further direction.

The chain-of-custody record provides sample descriptions and the date and time of sampling. Sampling procedures are addressed by NJDEP "Field Sampling Procedures Manual" requirements. Any discrepancies found by the reviewer must be noted on the data validation report. The non-conformance summary that is submitted by the laboratory is another source of general information. Notable problems with matrices, insufficient sample size for analysis or reanalysis, sample temperature and preservation and unusual events should be found here.

(D) Data Validation

1. Sample Holding Times

A. Objective

The objective is to ascertain the validity of results, based on the holding time of the sample from time of collection to time of analysis. From the standpoint of laboratory performance, the time of analysis is needed to determine compliance with the NJDEP modified USEPA SW-846, Final Update III Hexavalent Chromium method.

B. Requirements

The following holding time requirements were established by NJDEP.

Non Aqueous Samples for Hexavalent Chromium: seven (7) days from time of sampling to analysis.

Aqueous Samples for Hexavalent Chromium: 24 hours from time of sampling to

analysis

C. Evaluation Procedure

Actual holding times are established by comparing the sampling dates and times on the chain of custody with the dates and times of analysis found in the laboratory data. Exceeding the holding time for a sample may result in a loss of the Hexavalent Chromium. This occurs through any number of mechanisms, such as deposition on the sample container walls or chemical activity. Therefore, from a usability standpoint, when holding time violations occur, the results which are most severely called into question are those which fall below or close to the detection limit or a cleanup level.

D. Action

1) For nonaqueous samples, if the holding time is greater than seven days but less than or equal to nine days, then the sample concentration is qualified and flagged the data with a "J". If the holding time exceeds nine days, then all sample results are rejected "R".

2) For aqueous samples, if the holding time is greater than 24 hours but less than or equal to 48 hours, then the sample concentration is qualified and flagged the data with a "J". If the holding time exceeds 48 hours, then all sample results are rejected "R".

2. Instrument Calibration Curve

A. Objective

The objective in establishing compliance requirements for satisfactory instrument calibration is to ensure that the instrument is capable of producing acceptable quantitative data.

B. Requirements

1) The instrument must be calibrated daily (once every 24 hours) or each time the instrument is set up, whichever is more frequent.

2) The instrument standardization date and time must be included in the raw data.

3) A calibration blank and at least four (4) standards in graduated amounts and in the appropriate range (0.10 to 2.0 mg/L) are recommended in establishing the analytical curve.

4) The calibration curve must have a correlation coefficient of 0.995 or greater.

C. Evaluation Procedure

1) By checking the raw data, verify that the instrument was calibrated at the proper frequency.

2) Verify that the correct number of standards and calibration blanks was used.

3) Verify that the date and time of sample analysis was provided.

4) Verify that the correlation coefficient for the calibration curve was greater than or equal to 0.995.

5) Verify that if the correlation coefficient was less than 0.995, the laboratory analyzed a new calibration curve.

D. Action

1) If there are inconsistent time(s), date(s), or instrument IDs on the raw data sheets and reporting forms, the laboratory must be contacted and all inconsistencies must be resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data in question.

2) If the instrument calibration was not performed or calibrated daily, then all associated data are rejected "R".

3) If the correct number of instrument calibration standards was not analyzed then all associated data are qualified "J".

3) If the correlation coefficient for the calibration curve was less than 0.995, then all associated data are rejected.

3. Calibration Check Standard (CCS)

A. Objective

The CCS documents satisfactory instrument performance (calibration accuracy) during each analysis run.

B. Requirements

1) The CCS analyses must be performed at a minimum frequency of once every 10 samples during an analysis run. The CCS must be analyzed at the beginning of the run and after the last analytical sample.

2) The CCS should be at or near the mid range level of the calibration curve.

3) The same concentration for the CCS must be used throughout the sample analyses.

4) The CCS results must fall within the control limits of 90-110% of the true value.

5) The CCS must be independently prepared standard from a different source than that used for the initial calibration.

C. Evaluation Procedure

1) Review the supporting raw data to verify that the CCS was performed at the proper frequency.

2) Verify that the CCS was independently prepared and the standard used was at or near the mid range level of the curve.

3) Verify that the same CCS concentration was used throughout the analyses.

4) Verify that the standard used for performing the calibration verification met the acceptance criteria for 90-110%.

D. Action

1) If there are inconsistent time(s), date(s), or instrument IDs on the raw data sheets and reporting forms, the laboratory must be contacted and all inconsistencies must be resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify, or reject the data questioned.

2) If the CCS analysis was not performed, then all associated sample data are rejected “R”.

3) If the CCS analysis was not performed at the correct frequency, then all associated sample data are qualified "J".

4) If the CCS was not at or near the mid range level of the curve, then all associated sample data are qualified "J".

5) If the CCS concentration was not the same throughout the analysis, then qualify "J" all associated sample data if the concentration was within the calibration range and reject "R" all associated sample data if the concentration was not within the calibration range.

6) If the CCS analysis was performed but did not meet the % recovery requirements, use the following guidelines:

   a) If the CCS falls outside the acceptance windows but within the ranges of 80-89% or 111-120%, flag the positive hit data of associated samples as estimated (J). In the data validation report, give an indication to the data end user as to the bias of the results (i.e., if the CCS for an analyte is 115%, then it could be stated that the reported results for that analyte should be biased high.)

   b) If an analyte is not detected in a sample and the associated CCS result is greater than 110% but less than or equal to 120%, then the analytical sample determination is acceptable.

   c) If the analyte is not detected in a sample and the associated CCS result is less than 90% but greater than or equal to 80%, then the detection limit may be biased low. In the data validation report, note that the detection limit for that sample may be elevated and flag the data for these samples as estimated (UJ).

   d) If the CCS result is less than 80% or greater than 120%, this is indicative of severe analytical deficiencies and the data are rejected as unusable (R).

7) For a given CCS, the actions described in item 6) will affect the samples that are analyzed between the two acceptable CCSs that bracket the unacceptable CCS.

4. Calibration Blanks

A. Objective

Calibration Blanks are analyzed in order to establish that the instrument has no contamination or drifting problems, and to ensure that the instrument is capable of producing acceptable quantitative data.

B. Requirements

1) A Calibration Blank must be used in establishing the analytical curve.

2) The absolute value of the calibration blank should not exceed the Method Detection Limit (MDL).

3) A Calibration Blank must be analyzed before the initial instrument's calibration standards and after each CCS.

C. Evaluation Procedure

1) Review the supporting raw data to verify that the Calibration Blank analysis was performed and at the proper sequence.

2) Verify that the Calibration Blank absolute value was less than the MDL.

D. Action

1) If there are inconsistent time(s), date(s), or instrument IDs on reporting forms and raw data sheets, the laboratory must be contacted and all inconsistencies resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data in question.

2) If the absolute value of the Calibration Blank exceeds the MDL, then highly qualify "J" the data in all associated analytical samples.

3) If no Calibration Blank was run, all associated sample data are rejected "R".

5. Preparation/Reagent Blanks and Field Blanks

A. Objective

The assessment of results regarding blank analyses is for determining the existence and magnitude of contamination problems. The criteria for the evaluation of blanks apply to all blanks, including, but not limited to preparation/reagent blanks and field blanks. The responsibility for action in the case of unsuitable blank results depends upon the circumstances and the origin of the blank. If problems with any blank exist, all associated data must be carefully evaluated to determine whether there is an inherent variability in the data set or the problem is an isolated occurrence not affecting other data.

B. Requirements

1) The laboratory preparation/reagent blank is an in-house blank the laboratory is responsible for reporting.

2) At least one preparation/reagent blank, consisting of deionized distilled water, processed through each sample preparation and analysis procedure must be prepared and analyzed with every Sample Delivery Group (SDG), or for each batch of samples digested, whichever is more frequent. (Exception: If only soil samples were analyzed, an aqueous preparation blank is not required for the associated field blank.)

3) The minimum field blank requirement is as follows. There should be at least 1 field blank/matrix/per sampling date.

4) It should be noted that inorganic analysis for trip blanks is not required unless specifically requested by NJDEP on a site by site basis.

C. Evaluation Procedure

1) Review the results for the preparation/reagent blank(s) (raw data, strip charts, printer tapes, bench sheets, etc.) in order to verify that results were accurately reported.

2) Verify that the proper number of preparation/reagent blanks was analyzed.

3) Verify that the proper number of field blanks was analyzed, as per the request of the data end user.

4) Verify that the sample concentration is not corrected for any preparation/reagent blank, trip blank or field blank values.

D. Action

1) If there are inconsistent time(s), date(s), or instrument ID(s)on reporting forms and raw data sheets, the laboratory must be contacted and all inconsistencies must be resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data.

2) If any samples are not associated with a preparation/reagent blank, all data from the affected samples are rejected "R". (An aqueous reagent blank for the field blank is not required if only soil samples were analyzed).

3) If no field blanks were requested for analyses or if the incorrect number were collected and analyzed, note it in the data validation report.

4) If the preparation/reagent blank or field blank results were subtracted from associated sample results, add the applicable blank results to the sample results before proceeding to steps 6) and 7) below. The laboratory must be notified of the data reporting error and a revised data report package must be submitted.

5) If the sample concentration of Hexavalent Chromium is greater than ten (10) times the preparation/reagent blank, then no qualifications are necessary.

6) When the sample concentration of Hexavalent Chromium is less than or equal to ten (10) times the preparation/reagent blank, then the following actions are to be taken.

   a) If the concentration of Hexavalent Chromium in a sample is less than or equal to three (3) times the concentration of Hexavalent Chromium in the associated preparation/reagent blank, the presence of Hexavalent Chromium in the sample is negated due to laboratory contamination, as indicated by the preparation/reagent blank. The "B" qualifier must be reported with the analytical result.

   b) If the concentration of Hexavalent Chromium in a sample is greater than three (3) times the concentration of Hexavalent Chromium in the associated preparation/reagent blank, the presence of Hexavalent Chromium in the sample is considered "real". The "B" qualifier must be reported with the analytical result. The concentration must also be reported with the "J" qualifier and is quantitatively qualified due to preparation/reagent blank contamination.

   c) If the value of Hexavalent Chromium in the preparation/reagent blank is negative, then all positive values found in a field sample will be quantitatively qualified because of the possibility of a negative drift in the instrument and may be biased low.

   d) If the value of Hexavalent Chromium in the preparation/reagent blank is negative, then all non-detected values found in a field sample are reported "UJ" because of the possibility of a negative drift in the instrument and may give rise to a false negative (ND).

7) When the sample concentration of Hexavalent Chromium is less than or equal to ten (10) times the field blank concentration, then the following actions are to be taken.

   a) If the concentration of Hexavalent Chromium in a sample is less than or equal to three (3) times the concentration of Hexavalent Chromium in the

associated field blank, then the presence of Hexavalent Chromium in the sample is negated due to introduced contamination, as indicated by the field blank.

b) If the concentration of Hexavalent Chromium in a sample is greater than three (3) times the concentration of Hexavalent Chromium in the associated field blank, then the presence of Hexavalent Chromium in the sample is considered "real". The concentration must be reported with the "J" qualifier and is quantitatively qualified due to field blank contamination.

6. Predigestion Spike Sample Analysis (non aqueous samples only)

A. Objective

The spiked sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology.

B. Requirements

1) At least one spiked sample analysis must be performed on each group of samples of a similar matrix type (e.g., sediment, soil) and concentration (e.g., low, medium) for each digestion batch of samples or for each 20 samples received, whichever is more frequent.

2) If the spike analysis is performed on the same sample that was also chosen for the duplicate sample analysis, spike calculations must be performed using the results of the original sample analysis.

3) The analyte spike must be added before sample digestion andthe spike recovery must be within the control limits of 75-125%.

4) The predigestion spike concentration should be at 0.5 mg/L.

C. Evaluation Procedure

1) Verify that the proper number of spikes and the proper spike concentrations were used.

2) If spike analysis is performed on the same sample that was chosen for duplicate analysis, verify that the laboratory used the original sample results for calculations.

3) Spot check the raw data to verify that results were correctly calculated and reported on the spike analysis form. Predigestion spike percent recoveries (% R) are calculated as follows:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spike sample results
SR = Sample results
SA = Spike added

4) Verify that the spike recovery fall within the control limits of 75-125%.

5) Verify that a field sample and not a field blank was used for predigestion spike analysis as per NJDEP requirements.

D. Action

1) If there are inconsistent time(s), date(s), or instrument IDs on reporting forms and raw data sheets, the laboratory must be contacted and all inconsistencies resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data in question.

2) If no spike analysis was performed for non aqueous samples (i.e., either soil and/or sediment samples) or if a field blank was used, then all associated sample data are rejected "R".

3) If the frequency of the spike analysis exceeded 1 in 20 samples but was within 1 in 25, qualify "J" the data from samples 21-25.

4) If the frequency of a spike analysis exceeded 1 in 25 samples, reject "R" all sample data that follow the 25th sample.

5) If the wrong spike concentration was used, then qualify "J" that analyte(s) in all associated sample data.

6) The following guidelines are recommended for use in evaluating data usability when the spike recoveries do not fall within the control limits of 75-125%.

   a) If the spike recovery is > 125% and the reported sample results are less than the MDL, this data are acceptable for use.

   b) If the spike recovery is > 125% and the reported sample levels are greater than the MDL, then qualify the data "J" and give an indication in the data validation report as to the potential high bias of the results.

c) If the spike recovery is < 75% and the reported sample levels are greater than the MDL, then qualify the data "J". In the data validation report, give an indication as to the low bias of the results.

d) If an analyte is not detected in a sample and spike recovery is less than 75%, then the detection limit may be biased low. In the data validation report, note that the detection limit reported by the laboratory for that sample may be biased low. Flag the data for the associated samples as qualified "UJ".

7. Post Verification Spike Sample (PVS)

A. Objective

The PVS analysis is designed to verify that neither a reducing condition nor a chemical interference is affecting the analysis.

B. Requirements

1) At least one PVS analysis must be performed on each group of samples of a similar matrix type (e.g., water, soil) for each batch of samples or for each 20 samples received, whichever is more frequent.

2) As per NJDEP requirements, samples identified as field or preparation/ reagent blanks cannot be used for PVS analysis.

3) If the PVS analysis is performed on the same sample that was also chosen for the duplicate sample analysis, PVS spike recovery calculations must be performed using the result of the original sample analysis.

4) The sample chosen for PVS should be spiked at 150 ug/L or twice the sample concentration, whichever is greater.

5) The PVS spike recovery must be within the control limits of 85-115%.

6) If the PVS recovery is less than 85%, then reanalyze the PVS to determine if the low spike recovery is due to a reducing agent.

7) When the sample concentration is less than the MDL, use 0 for the sample results only for the purpose of calculating the % recovery.

C. Evaluation Procedure

1) Verify that the PVS analysis was performed at the proper frequency (1 for every 20

samples) and that the proper PVS concentration was used.

2) Verify that a field sample and not a field blank or preparation/ reagent blank was used for PVS analysis as per NJDEP requirements.

3) Spot-check the raw data to verify that PVS recovery result was correctly calculated and reported. PVS percent recoveries (% R) are calculated as follows:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where: SSR = PVS sample result
SR = Sample result
SA = Spike added

4) Verify that the PVS recovery results fall within the specified limits of 85-115%.

5) Verify that the PVS was reanalyzed if the recovery was less than 85%.

6) Verify that when the addition of a PVS to a sample extends the concentration beyond the calibration range, a dilution was performed.

D. Action

1) If there are inconsistent time(s), date(s), or instrument IDs on reporting forms or raw data sheets, the laboratory must be contacted and all inconsistencies resolved. If the reviewer is unable to resolve any of the discrepancies, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data in question.

2) If no PVS analysis was performed for either soil and/or aqueous samples, all associated sample data are rejected "R".

3) If a field blank or preparation/ reagent blank was used for PVS analysis, then reject “R” all associated sample data.

4) If the frequency of the PVS analysis exceeded 1 in 20 samples but was within 1 in 25, qualify "J" the data from samples 21-25.

5) If the frequency of a PVS analysis exceeded 1 in 25 samples, reject "R" all sample data that follow the 25th sample.

6) If the wrong PVS concentration was used, qualify "J", Hexavalent Chromium in all associated sample data.

7) The following guidelines are recommended for use in evaluating data usability when the PVS recoveries do not fall within 85-115% limits:

a) If the PVS recovery is > 115% and the reported sample results are less than the MDL, the data are acceptable for use.

b) If the PVS recovery is > 115% and the reported sample levels are greater than the MDL, then flag data as estimated "J" and give an indication in the data validation report as to the potential high bias in the results.

c) If the PVS recovery is less than 85% the following actions are taken:

i) If no reanalysis was performed, and the reported sample levels are greater than the IDL, then the data are qualified "J". In the data validation report, give an indication as to the low bias of the results.

ii) If no reanalysis was performed, and the reported sample levels are less than the IDL then the detection limit is qualified “UJ”. In the data validation report, note that the detection limit reported by the laboratory for that sample may be biased low.

iii) If the laboratory reanalyzes the aliquot and the recovery is within 85-115% recovery limits, no action is needed.

iv) If the reanalysis is still outside the (recovery) limits, then qualify "J" all associated samples.

8) If the laboratory failed to make a dilution to any PVS that exceeded the calibration range, qualify " J" all associated samples.

8. Duplicate Sample Analysis

A. Objective

The duplicate sample analysis is used to evaluate the precision of the method for Hexavalent Chromium. The data reviewer can use the results of the duplicate analysis as an indicator of the precision of the sample results.

B. Requirements

1) One duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and for each batch of samples or for each 20 samples received, whichever is more frequent.

2) As per NJDEP requirements, samples identified as field blanks or preparation/reagent blanks cannot be used for duplicate sample analysis.

3) Duplicate results must be reported on duplicate form in ug/L for aqueous samples and mg/Kg dry weight basis for solid samples.

4) A control limit of 20 % Relative Percent Different (RPD) shall be used for aqueous samples and for nonaqueous samples whose values are greater than or equal to 8 ppm.

The RPD for Hexavalent Chromium is calculated as follows:

$$RPD = \frac{S - D}{(S + D)/2} \times 100$$

Where: RPD = Relative Percent Difference
S = First sample value (original)
D = Second sample value (duplicate)

5) A control limit of $\pm$ 2 ppm shall be used:

a) If both sample values are less than 8.0 ppm;

b) If only one sample value is less than 8.0 ppm.

C. Evaluation Procedure

1) Verify that duplicate samples were analyzed for each matrix type and at the proper frequency.

2) Spot-check the raw data to verify that the results have been correctly reported on the duplicate form.

3) Verify that a field sample was used for duplicate analysis as per NJDEP requirements.

4) Verify that the correct control limits were used.

D. Action

1) If there are inconsistent time(s), date(s), or instrument IDs on reporting forms and

raw data sheets, the laboratory must be contacted and all inconsistencies resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data in question.

2) If no duplicate sample was analyzed for either soil and/or aqueous matrices, then all associated sample data are rejected "R".

3) If a field blank or preparation/reagent blank was used for duplicate analysis, then all associated sample data are rejected “R”.

4) If the frequency of the duplicate analysis exceeded 1 in 20 samples but was within 1 in 25, qualify "J" the data from samples 21-25.

5) If the frequency of a duplicate analysis exceeded 1 in 25 samples, reject "R" all sample data that follow the 25th sample.

5) If the duplicate sample analyses results for Hexavalent Chromium fall outside the control windows of 20% RPD or $\pm$ 2 ppm, whichever is appropriate, the results in all associated samples of the same matrix type should be flagged as estimated "J".

9. Laboratory Control Sample Analysis (LCS) (non aqueous samples only)

A. Objective

The laboratory control sample analysis (LCS) is designed to serve as a monitor of the efficiency of the digestion procedure. The inability of the laboratory to successfully analyze a known QC check sample (LCS) is indicative of an analytical problem related to a digestion/sample preparation procedures and/or instrument operations. This analysis is currently an option for the laboratory.

B. Requirements

1) One LCS must be analyzed for every SDG of non aqueous samples received or for each batch of samples digested, whichever is more frequent. Results for each Hexavalent Chromium should be reported on the LCS form.

2) The LCS must be prepared by the laboratory.

3) The LCS percent recoveries (%R) must fall within the control limits of 80% -120%.

C. Evaluation

1) Verify that the LCS was analyzed and at the proper frequency.

2) Review the LCS form and verify that the results fall within the specified control limits.

3) Spot check the raw data (printouts, strip chart, bench sheets) to verify the reported recoveries on the LCS form.

D. Action

1) If there are inconsistent time(s), date(s), or instrument IDs on reporting forms and raw data sheets, the laboratory must be contacted and all inconsistencies resolved. If the reviewer is unable to resolve any discrepancies with the laboratory, then the reviewer must determine on a case by case basis whether to accept, qualify "J", or reject "R" the data.

2) If the frequency of a LCS analysis exceeded 1 in 20 samples, qualify "J" the data from the 21st sample on.

3) If the LCS was not within control limits, qualify "J" all associated samples.

10. Sample Result Verification

A. Objective

The sample results verification process checks the correctness of the data acquisition, computation, transcription and the validity of the calibration curve construction.

B. Requirements

1) It is implicit within the USEPA SW-846 Final Update III document that all required data reduction, reporting and documentation be performed and presented in such a manner so as to ensure the data package is both complete as well as free of computational and/or transcription errors.

2) Percent solids determinations are required for all non-aqueous samples. Sample dry weight corrections are made using the percent solids results.

3) NJDEP modified methods 3060 & 7196A require pH adjustments for each sample and their final readings recorded in a laboratory notebook.

   a) Method 3060-pHs of all analytical solutions for non-aqueous sample must be adjusted within a range of 7.0 - 8.0.

b) Method 7196A - pHs of all analytical solutions must be adjusted within a range of 1.6 - 2.2.

4) NJDEP modified method 3060 requires that the digestion solution temperature must be monitored at 30 minutes and 60 minutes and recorded in the laboratory notebook for one sample.

C. Evaluation Procedure

In addition to the evaluation procedures previously outlined within this document, the specific elements of the data validation process should include the following:

1) Examine the raw data for any anomalies (i.e., negative absorbance, omissions, etc.).

2) Verify that there were no computational errors in sample concentration by re-calculating the results for Hexavalent Chromium in a percentage of samples.

3) Calculations

a) For aqueous samples, calculate the Hexavalent Chromium results as follows:

Hexavalent Chromium in mg/L = A x E

Where: A = concentration from the calibration curve in mg/L.
E = Dilution (if necessary)

b) For solid samples, when concentrations are reported as mg/Kg on a dry basis use the following formula.

$$\text{mg Hexavalent Chromium/Kg sample} = \frac{A \times B \times E}{C \times D}$$

Where: A = concentration from the calibration curve in mg/L.
B = Final digested volume in liters.
C = Wet weight of sample in kilograms.
D = % Solids/100
E = Dilution (if necessary)

4) Verify that there were no transcription errors by checking the raw data versus the analytical result summary sheet.

5) a) Verify that percent solids analysis for all non-aqueous samples was

performed.

b) Verify the percent solids determinations by spot checking the laboratory results using the following formula.

$$\% \text{ Solids} = \frac{\text{Sample dry weight}}{\text{Sample wet weight}} \times 100$$

6) Verify that the laboratory has provided pH readings for methods 3060 and/or 7196A.

7) Verify that the pH reading(s) were within the specified range(s) for each sample.

8) Verify that the temperature readings were provided, and were within a temperature range of 90 – 95 degrees centigrade.

D. Action

1) If any raw data anomalies were found, the reviewer should use judgement on how the sample data would be affected.

2) If differences are identified between the laboratory reported result and the reviewer calculated result, the following actions should be taken:

a) If the laboratory reported result is within 10% of the reviewer calculated result and the difference could be attributed to rounding, no corrective action is required.

b) If the laboratory reported result differs by 10% from the reviewer calculated result, but not attributable to rounding, try to determine the source(s) of error. If this cannot be determined, the laboratory should be contacted about the sample result discrepancy. If an error is confirmed, request submission of corrected data sheets from the laboratory. Summarize all actions taken in the Data Validation Report.

3) Transcription errors that affect the data shall be noted in Data Validation Report. Also, the laboratory shall be contacted and the submission of corrected data sheets shall be requested.

4) If the % Solids data were not provided then note the deficiency in the data validation report. The results are qualified and possibly biased low.

5) If the pH readings are not provided, then contact the laboratory. The data are conditionally rejected pending satisfactory verification of the pHs.

6) If the laboratory failed to record the pH data in a laboratory notebook, then the following actions are taken:

   a) The data are qualified with an unknown bias if the positive results exceed the clean-up action level.

   b) The data are suspect if the positive results are below the clean-up action level.

   c) The "non-detected" data are rejected because the possibility of false NDs exists.

7) If the temperature readings are not provided, then contact the laboratory. The data are conditionally rejected pending satisfactory verification of the digestion solution temperature.

8) If the laboratory failed to record the digestion solution temperature in a laboratory notebook, then the following actions are taken:

   a) The data are qualified with an unknown bias if the positive results exceed the clean-up action level.

   b) The data are suspect if the positive results are below the clean-up action level.

   c) The "non-detected" data are rejected because the possibility of false NDs exists.

APPENDIX I - GLOSSARY OF TERMS

ABSORBANCE - a measure of decrease in incident light passing through a sample into the detector. It is defined mathematically as:

$$A = \frac{I\ (solvent)}{I\ (solution)} = \log \frac{Io}{I}$$

Where, I = radiation intensity

ALIQUOT- a measured portion of a field sample taken for analysis.

ANALYSIS DATE/TIME - the date and military time (24-hour clock) of the injection of the sample, standard, or blank into the analysis system.

ANALYTE - the element or ion an analysis seeks to determine; the element of interest.

AUTOZERO - zeroing the instrument at the proper wavelength. It is equivalent to running a standard blank with the absorbance set at zero.

AVERAGE INTENSITY - the average of two different injections (exposures).

BACKGROUND CORRECTION - a technique to compensate for variable background contribution to the instrument signal in the determination of trace elements.

BATCH - the basic unit for analytical quality control is the analytical batch. The analytical batch is defined as 20 samples or less which are analyzed together with the same method sequence and the same lots of reagents and the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g. groundwater, sludge, ash, etc.).

CALIBRATION - the establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type of acid or concentration of acids as used in the sample preparation.

CALIBRATION BLANK - a volume of digestion solution/distilled water.

CALIBRATION CHECK STANDARD - analytical standard run every 1O analytical samples to verify the calibration of the analytical system.

COEFFICIENT OF VARIATION (CV) - the standard deviation as a percent of the arithmetic mean.

CONTROL LIMITS - a range within which specified measurement results must fall to be

compliant. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that noncompliant data be flagged.

CORRELATION COEFFICIENT - a number (r) which indicates the degree of dependence between two variables (concentration - absorbance). The more dependent they are the closer the value to one. Determined based on the least squares line.

DAY - unless otherwise specified, day shall mean calendar day.

DIGESTION LOG - an official record of the sample preparation (digestion).

DUPLICATE - a second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

FIELD BLANK - any sample submitted from the field identified as such a blank.

HOLDING TIME - the elapsed time expressed in days from the date of sample collection until the date of its analysis.

Holding time = (sample analysis date - sampling date)

INDEPENDENT STANDARD - a laboratory-prepared standard solution that is composed of Hexavalent Chromium from a different source than that used in the standards for the initial calibration.

INJECTION - introduction of the analytical sample into the instrument excitation system for the purpose of measuring absorbance, emission or concentration of an analyte. May also be referred to as exposure.

INSTRUMENT DETECTION LIMIT (IDL) - determined by multiplying by three the standard deviation obtained for the analysis of a standard solution (each analyte in reagent water) at a concentration of 3x-5x IDL on three nonconsecutive days with seven consecutive measurements per day.

INTERFERENTS - substances which affect the analysis for the element of interest.

MATRIX - the predominant material of which the sample to be analyzed is composed.

MATRIX SPIKE - aliquot of a sample (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

METHOD DETECTION LIMIT (MDL) - The minimum concentration of a substance that can be measured and reported with 99 % confidence that the analyte concentration is greater than zero

and is determined from analysis of a sample in a given matrix containing the analyte. The procedures for determining the MDL are located in Chapter 1 of SW-846.

PREPARATION BLANK (reagent blank, method blank) - an analytical control that contains distilled, deionized water and reagents, which is carried through the entire analytical procedure (digested and analyzed). An aqueous method blank is treated with the same reagents as a sample with a water matrix; A solid method blank is treated with the same reagents as a soil sample.

PROTOCOL - a compilation of the procedures to be followed with respect to sample receipt and handling, analytical methods, data reporting and deliverables, and document control.

ROUNDING RULES - if the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example, 11.443 is rounded off to 11.44.

If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example, 11.446 is rounded off to 11.45.

If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number. As an example, 11.435 is rounded off to 11.44, while 11.425 is rounded off to 11.42.

If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.

RUN - a continuous analytical sequence consisting of prepared samples and all associated quality assurance measurements as required by the USEPA, SW-846.

SOIL - synonymous with soil/sediment or sediment as used herein.

SPECTROMETER - An instrument with an entrance slit, a dispersing device, and one or more exit slits, which measurement are made at selected wavelengths within the spectral range, or by scanning over the range.

STOCK SOLUTION - a standard solution which can be diluted to derive other standards.

WET WEIGHT - the weight of a sample aliquot including moisture (undried).